HIGH RESOLUTION EUV EMISSION SPECTROSCOPY OF THE N_2 C' V' = 3 AND 4 LEVELS BY ELECTRON IMPACT

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ABSTRACT

A high resolution $36\,m\text{Å}$ (FWHM), optically thin emission study of the N_2 c' $^1\Sigma_u^+$ (4,3) and (3,2) Rydberg bands excited by electron impact at 100 eV has been completed in the extreme ultraviolet (EUV). A model of the perturbed rotational line intensity distribution of the bands shows the effects of electronic state mixing between the c' $^1\Sigma_u^+$ Rydberg state and the b' $^1\Sigma_u^+$ valence state. By normalizing the model to the published predissociation yield for J' =9 the laboratory spectrum can be used to determine the predissociation yields for each rotational level of v' =3 and 4. Based on a 15% accuracy of the model fit to the measured signal intensities it is found that the predissociation yield of each c' rotational level increases as the percentage of b' $^1\Sigma_v^+$ character increases. The mean predissociation yields for c' v'= 3 and 4 levels are 0.42 and 0.54, respectively at 300 K. The J'-dependent predissociation yields indicate that the emission cross section is a function of temperature. The remainder of the bands forming the v" progressions (v"= O to 5) from v'= 3 and (v"= O to 6) from v' = 4 were studied at $64\,m\text{Å}$ (FWHM) resolution. Using this composite spectrum of the two progressions the electron impact emission cross sections of the N_2 c' v' =3 and 4 levels at 300 K were determined and compared to previous results.

INTRODUCTION

The rotational line structure of the N_2 c' $^1\Sigma_u^+$ band system has been studied by a variety of techniques. We have recently reported the high resolution structure of the $N_2(c'^1\Sigma_u^+$ (0,0)) band in an optically thin electron-impact emission experiment (Shemansky *et al* 1995; Ajello *et al* 1996b). A model of the rotational line intensities using the line positions measured by Yoshino and Tanaka (1977) shows good agreement with the data by including a modest amount predissociation yield of -140/0 at room temperature. In an earlier work at medium resolution (Ajello et *al* 1989) it was concluded that a similar predissociation yield may be applicable for the higher vibrational levels as well. Complementary high resolution emission spectra by Roncin e*t al* (1987a,b) with a discharge source indicated few effects from predissociation. These researchers at the Meudon Observatory have published band origins for the N_2 c' $^1\Sigma_u^+$ band system. At the same time using photofragment spectroscopy Walter *et al* (1994) have measured predissociation yields directly as well as lifetimes for some of the v' levels of the c' state, in particular the c' $^1\Sigma_u^+$ (v'= 3,4) rotational levels. Kam *et al* (1989) have also studied v'=3 and measured the lifetimes of the c' $^1\Sigma_u^+$ (J= 9, 13; v'= 3) rotational levels by studying absorption linewidths. Helm et *al* (1993) have measured the lifetimes of all the c' $^1\Sigma_u^+$ (v'= 4) rotational levels. The lifetimes decrease from 0.2 ns for J'=7 to 0.064 ns for J'=15 as the c' state acquires more b'

character. The implication of the combined lifetime and photofragment spectroscopy studies is that magnitude of c' $^1\Sigma_u^+$ - b' $^1\Sigma_u^+$ mixing determines the predissociation yield. The controversy spurred by the previous works as to the exact amount of weak predissociation has led to suggestions that high resolution emission spectra of the rotational manifold may go a long way to solving this problem (Walter *et al* 1994; Kam *et al* 1989). For this purpose we have received from the Meudon researchers a list of the unpublished rotational line position for the P and R-branches of the N_2 c' $^1\Sigma_u^+$ ((4,3) and (3,2)) Rydberg bands to enable the intensity modeling with wavelength of rotational structure in this work.

Analysis of the experimental data would not be possible without assistance from theoretical studies of the c' $^1\Sigma_u^+$ Rydberg state and b' $^1\Sigma_u^+$ valence state interaction. The pivotal work was performed by Stahel *et al* (1983). Consideration of the homogeneous perturbation between $^1\Sigma_u^+$ states allowed calculation of the perturbed and deperturbed electronic transition moments from the electron energy loss data of Geiger and Schröder (1969). As an extension of this work, Helm *et al* (1993) calculated the percentage electronic-rotational mixing for each rotational level of v'=4. Similarly, Edwards *et al* (1995) have calculated for v' =3 the percentage electronic character of the c' $^1\Sigma_u^+$ and b' $^1\Sigma_u^+$ rovibronic states.

We present in this paper a brief discussion of the experimental technique followed by an analysis of the high resolution spectra measured for

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the v" progressions (v"= O to 5) from v'= 3 and(v''= O to 6) from v' = 4. The analysis indicates that the mean predissociation yield is a function of temperature as the low-lying rotational levels (J' < 8) are weakly predissociated with a smaller predissociation yield than the high rotational levels (J ' - 14).

EXPERIMENTAL.

The experimental system has been described by Liu *et al* (1995) and Ajello e f *al* (1995a,b; 1996a,b). In brief, it consists of a high-resolution 3-meter U V spectrometer in tandem with an electron impact collision chamber. A resolving power of 25,000 (36 mÅ FWHM) is achieved by operating the spectrometer in second order. The rotational line structure was measured under experimental conditions that ensure linearity of the signal with electron beam current and background gas pressure.

RESULTS

The spectrum was measured in a crossed beams mode at 100 e V electron impact energy. The N_2 c' $^1\Sigma_u^+$ ((3,2) and (4,3)) Rydberg bands in the EUV span the wavelength range from 943 to 946 Å and are shown in Fig. 1. The wavelengths for the fine structure lines were provided b y

Roncin and Launay (private communication, 1997). Spectra measured at a resolution of 64 mÅ (FWHM) for the v" progressions (v" = O to 5) for v' = 3 and (v" =0 to 6) for v' =4 are shown in Fig. 2a and Fig. 2b. These spectra represent an important set of data required to obtain accurate emission cross sections for the v'=3 and 4 vibrational levels. For the first time, it is possible to resolve features in the EUV for the N_2 c' v'=3, 4 levels. It is observed that the N_2 c' $^1\Sigma_u^+$ (v' =3, v" =2 and 4) and (v' =4, v" =3 and 5)) Rydberg bands are unblended, while the remainder of the N_2 c' $^1\Sigma_u^+$ (v'=3 and 4) Rydberg bands of the progression overlap with NI resonance lines. Features in the EUV spectrum were identified in our previous medium resolution work (Ajello et al 1989). The emission cross section for each vibrational band is given in Table 1. These cross sections are based upon the cross sections from our earlier work (Ajello et al 1989) with a correction for the effects of blending. The amount of NI multiplet line blending is determined for N_2 c' $^1\Sigma_u^+$ (3, 3) by smoothly extending the rotational structure of the P-branch in the regions of the NI lines. The amount of NI multiplet line blending for N_2 c' $^1\Sigma_u^+$ (4, 4) is more difficult to measure because of the fortuitous alignment of the R-branch band head with the NI line at 96.504 nm. We estimate the blending by assuming the ratio of cross sections for the (4,4)/(3,3) bands is the same as the (4,3)1(3,2) and (4,5)/(3,4) band ratios. This ratio for both unblended bands is nearly 1.5. We removed the blending for other bands in a similar way, utilizing   a knowledge of the true rotational structure. The revised

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vibrational level cross sections are lower by 16% for v'=3 and 27% for v'=4 from our 1989 work (Ajello *et al* 1989). Despite this revision emission remains a very effective mechanism for depopulating the v'=3 and 4 vibrational levels.

THEORETICAL. BACKGROUND AND MODELING

The line intensity of a rovibronic band is given by

$$I(v', v'': J', J'') = g(v',J') A (v', v'': J', J'')/A(v': J') \tag{1}$$

Where the single prime and double prime refer to upper and lower state levels, respectively, and summation over any missing index is assumed. v and J refer to vibrational and rotational quantum numbers. $A(v', v'': J', J'')$ is the Einstein transition probability between two levels J' and J", and $A(v': J')$ is the total transition probability. $A_{,n'}(v': J')$ is the total emission probability and $A(v': J')$ is defined by

$$A(v': J') = A_{,n'}(v': J') + \Gamma (v', p: J') \tag{2}$$

where p refers to the predissociation yield at a rate, r, from fine structure level (v', J'). $g(v', J')$ is the excitation rate and is given by

$$g(v',J') = F\,Q(v''=0,\ v':\ J'',J')\,N(v'',J'') \tag{3}$$

where F, $Q(v''=0,\ v':\ J')$ and $N(v'',\ J'')$ are the electron flux, excitation cross section and ground state population, respectively. In the Born limit we write

$$Q(v''=0,\ v') \propto A(v',v''=0)\ \lambda_{mean}^{3}(v''=0,v') \tag{4}$$

and

$$Q(v''=0,\ v':\ J',J'') = Q(v''=0;\ v')\ S(J',J'')/(2J''+1) \tag{5}$$

When two states of the same symmetry interact, interference affects the rotational transitions out of a common mixed eigenstate in the same way (Lefebvre-Brion and Field, 1986). In this case the mixed transition probability can be written

$$A(\ v',\ v''=0:\ J',J'') \propto S(\ J',\ J'')[C_1 P_{10}(v',\ v''=0) \pm C_2\mu_{20}(v',v''=0)]^{2} \tag{6}$$

and

$$A(\ v',v''=0) \propto \{C_1^{2}\ \mu_{10}^{2}(v',\ v''=0)\ +\ (1-C_1^{2})\ \mu_{20}^{2}(v',\ v''=0)\ \pm$$

$$2\,C_1(1-C_1^{2})^{1/2}\ \mu_{10}\mu_{20}\} \tag{7}$$

where μ_{10} is the vibronic transition moment between the ground and b'

states and μ_{20} is the vibronic transition moment between the ground and c'

states. Cl and C_2 are eigenvector components tabulated as a function of J' by

Edwards *et al* (1995) for c'(3) ~ b'(10) and by Helm *et al* (1993) for c'(4) -

b'(13). Stahel *et al* (1983) have shown that for both the b'(10)~c'(3) and

b'(13)~c'(4) interactions $\mu_{10} >> \mu_{20}$. The band strength (the square of the dipole

transition moment) can be expressed as

$$\mu^2 = q_{v'v''} R_e^2 \tag{8}$$

where $q_{v'v''}$ is the Franck-Condon factor and R_e^2 is the square of the electronic

transition moment. We have previously shown that the Franck-Condon

factor for c'(3) and c'(4) from the ground state, v''=0, is negligibly small. The

excitation of the c'(4) occurs principally through interaction with the b' state.

The b'(v'=10,13) levels lie 35 and 31 meV above the c'(v'=3, 4) levels,

respectively. The perturbed transition probability is given by

$$A(v',v''=0: J', J'') \propto S(J', J''){C_1(J')^2 \mu^2_{10} (v', v''=0)} \tag{9}$$

Emission from the c'(v'=3,4) levels is only observed because of the intensity

borrowed from the b'(v'=10,13) levels. The b' state also takes part in the

predissociation process. It is responsible for predissociation of the c'(v'=3, 4) levels to the continuum.

The emission branching ratio involves a transition to the v''=3 and v''=2 levels for c' $^1\Sigma_u^+$ (4,3) and (3,2) bands, respectively. The emission branching ratio for any rotational line in the P or R-branch of band (v'; v'') can be written

$$\omega = A(\ v'/v'':\ J',J'')/A(v':J') \tag{lo}$$

In terms of an emission yield, $\eta_E(J)$, the branching ratio can be rewritten

$$\omega = A(\ v',v'':J',J'')\ \eta_E\ (v',J')/A_{em}(v':J')$$

where

$$\eta_E(v',J') = A_{em}(v':\ J')\ /A((v':\ J'). \tag{11}$$

We can expand the term $A(v',v'':J',J'')/A_{em}(v':\ J')$ in terms of the two perturbing states which both have $^1\Sigma_u^+$ symmetry.

$$A(\ v'/v'':\ J',J'')/A_{em}(v':\ J\ ') = S(\ J',\ J'')\{C_1^2\mu^2_{10}\ (v',\ v'') + (1-C_1^2)\mu^2_{20}\ (v',$$

$$v'')\ \pm 2\ C_{1+}\ (1-C_{1+}^2)^{1/2}\mu_{10}(v',\ v'')\ \mu_{20}(v',\ v'')\ \}/[\sum_{v'',J''=\pm1} S(\ J',\ J'')\{C_1^2\ \mu^2_{10}\ (v',\ v'') +$$

$$(1-C_1^2)\mu^2_{20}(v',v'') \pm 2\ C,\ (1-\ C_1^2)^{1/2}\ \mu_{10}\ (v',\ v'')\ \mu_{20}\ (v',\ v'')] \tag{12}$$

There is a simplification in the branching ratio calculation based on the Franck-Condon factors for the perturbing states involved. For both the c' $^1\Sigma_u^+$ v'=3 and 4 levels the leading terms in the downward transition emission transition probability, $A_{em}(v';J')$, in the denominator of eq. 11 arise from the central members of the v' sequences ($\Delta v=0, \pm 1$) . Table 1 shows the emission cross sections of the Av=O, ± 1 sequences for v'=3 and 4 represent 82 and 73"/0, respectively, of the total emission from these levels. Except for a small contribution to the v" progressions from v"=O and 1, the radiative transitions from v'=3 and 4 are strongly c' - X. For example, the c'(4,3) and (3,2) bands can be compared to the corresponding b'(13,3) and b'(10,2) bands. The b'(13,3) and b'(10,2) bands have Franck-Condon factors to the ground state that are much less than the analogous transitions for the c' bands. The Franck-Condon factors are shown in Table 1. For the c'(3,2) and b'(10,2) bands the set of Franck-Condon factors are 0.22 and 0.032, respectively, and for the c'(4,3) and b'(13,3) bands the set of Franck-Condon factors are 0.26 and 0.031. If we assume (as in Shemansky *et al* (1995)) that the two states have equal electronic transition moments then we may write with these two approximations

$$\omega = (S(J'/J") \eta_F(v',J')q_{2,0,v'v"}R_{e2,0}^2\} / \sum_{v",J"=\pm 1} S(J', J") \ q_{2,0,v'v"}R_{e2,0_2}, \qquad (13).$$

We show the model spectrum of the two N_2 Rydberg bands, c' $^1\Sigma_u^+$ (4,3) and (3,2), in Fig. 3 together with the data. By including a J'-level dependent

predissociation yield in the model, η_P (v', J') = 1- η_t (v', J'), an excellent fit to the laboratory spectrum can be obtained. Table 2 compares the experimental intensities in Fig. 3 with the modeled intensities using the eigenvector components of Edwards *et al* (1995) for c'(3) and Helm *et al* (1993) for c'(4). In both cases the percentage b' character increases with J' reaching 50% by J'=12 for v'=3 and by J'=14 for v'=4. The required predissociation yields are given in Table 2 along with the eigenvector components for b' percentage character, C_1^2. The predissociation yields for J' > 14 are estimated and are not observed in our spectra for T = 300 K. The predissociation yields are normalized to J'=9 from the work of Walter *et al* (1994). It is seen that the predissociation yields decrease with J' from 65°/0 at J'~15 to~30% for J'~5 for v'=3. For v'=4 we find that the predissociation yields decrease from 95% at J' -15 to -20 % at J'~5. The fit to the data is achieved mainly through modeling the P-branch, which clearly reveals the rotational structure of the band. The model without predissociation would not fit the data. The model of the rotational line intensities without predissociation would be too intense at large J'. Values of the predissociation yield for J' < 4 are uncertain by a factor of 2.

THE EMISSION CROSS SECTIONS OF THE v ' =3 AND 4 PROGRESSIONS

It is evident from the previous medium resolution work in emission (Ajello *et al* 1989; James *et al* 1990) that the c' v'=3,4 vibrational levels have a large emission cross section despite unfavorable Franck-Condon factors from the ground state, v"= O. Prior to this work, the early electron energy loss data of Geiger and Schröder had already showed that the relative excitation cross sections to these levels are quite high. The medium resolution emission work had indicated that the predissociation yield of these levels was quite small, less than 10%. However the work was troubled by blending from other emission features from N_2, particularly N1 lines. This deficiency was made more poignant by the recent set of publications by the group at SRI making use of photofragment spectroscopy and line width determinations. Helm et al (1989) showed that the line width of c' v'= 4 rotational levels increased with increasing rotational quantum number. Predissociation is clearly important for the c' -state. Walter et *al* 1994 were able to proceed a step further. They were able to measure the predissociation yields for certain J' levels of c' v'=3,4. They showed that the predissociation is greater than 50% for J'= 9,13 of v'=3 and for J'= 9 of v'=4. They inferred from these results and measurements on other rotational levels of other states that predissociation is the dominant decay path for all Rydberg and valence states of singlet ungerade character that lie at energies above 13.6 eV, the $N(^2P^0) + N(^4S^0)$ dissociation limit.

As we have pointed out, it became important to remeasure the entire c'
v'=3,4 v" progressions at high resolution to remove errors in the emission
cross section determination from blending. We list in Table 1 the revised
cross sections, compared to our earlier 1989 results for v"=O to 6.

We also list in Table 1, for the sake of this discussion, the measured
emission branching ratios and the Franck-Condon factors between v'=3 and 4
of the c' state to the v" levels of the ground state, together with the Franck-
Condon factors between v'= 10 and 13 levels of the b' state to some of the v''
levels of the ground state. The Franck-Condon set for b' is incomplete, since
the band system is very broad in v". The strongest emission from v'=3 is the
(3,2) band and the strongest emission from v'= 4 is the (4,3) band. Without the
perturbation the Franck-Condon factors would predict that the (3,3) and (4,4)
bands would be the strongest. The non-adiabatic interaction of electronic-
nuclear coupling leads to the intensity distribution that is observed.

CONCLUSIONS

The principal result of this paper is an analysis of the high resolution
(FWHM = 36 mÅ), optically thin emission spectrum of the N_2 c' $^1\Sigma_u^+$ (4,3) and
(3,2) Rydberg bands in the extreme ultraviolet (EUV) by electron impact
excitation at 100 eV. A model of the rotational structure of these two bands
yielded an estimate of the J' -dependent predissociation yields. The two sets of

v" progressions originating from v' =3 and 4 were measured at a resolution of 64 mÅ (FWHM). The spectral data can be explained by a rotational emission model that attributes the excitation process to favorable Frank-Condon factors from the ground state to b'-state v'=1O and 13 vibrational levels and a concomitant homogeneous perturbation between the b' and c'-states. The nonadiabatic coupling between the two states shortens the lifetime of the c'-state over that for pure spontaneous radiation, and the amount of b' character inherent in the c' state controls the predissociation yield. It is apparent from our results in Table 2 that the predissociation yield is greater than 50% for J' = 9 of v' =3 and J'=8 of v' =4, although we can not acquire any information for J' > 14. This important information on high J' will be determined by photofragment spectroscopy. The mean predissociation yield for a Boltzmann distribution is a strong function of temperature. We show in Fig. 4 a calculation of the mean predissociation yield as a function of temperature for a Boltzmann thermal distribution of the molecules populating the rotational levels. The observed emission from the c' state v' =3 ,4 levels will decrease as the temperature of the gas increases. At 300 K the mean predissociation yield is 42% for v'=3 and 54% for v'=4. For temperatures below 250 K the emission yields of both v'= 3 and 4 are larger than 50%. The results give an important corollary to planetary atmospheres modeling. The emission cross section of each vibrational level of N_2c' will change with temperature from very small in the Earth's atmosphere where temperatures approach 1000 K to much larger in the atmospheres of Triton and Titan

where temperatures are about 50-200 K. The results establish a trend of increasing mean predissociation yield with vibrational level by including i n the study the mean 300 K predissociation yield of 15% from our work on the c' v'=0 level (Shemansky et *al* 1995). The other strong levels, v'= 2 and 6, also need to be studied at high spectral resolution.

The results of this study can be used to resolve the controversy concerning the percentage yield of emission and predissociation. The two, at first glance, disparate results from the emission (Ajello *et al 1989*; Roncin *e t al* 1987a,b) and photofragment/absorption line width experiments (Walter e *f al* 1994; Kam *et al* 1989; Helm *et al* 1993 can be explained by referring to Table 2. The predissociation yield increases as a sharp function of increasing J' and high temperature will enhance the mean predissociation yield. Finally, it can be pointed out that the excitation cross section at 100 eV can be calculated based on the emission cross section and the mean predissociation yield at 300 K. Thus the total excitation cross section becomes 10.0 x 10^{-19} cm^2 for v'=3 and 21.5 x 10^{-19} crn^2 for v' =4. Although these absolute cross sections are dependent on the normalization used in constructing Table 2, the spectra obtained in this study are the first electron impact spectra to separate the effects of blending of the b'(v' =10 and 13) levels with the c'(v' =3 and 4) levels, respectively. The ratio of excitation cross sections of c'(4) /c'(3) obtained here is 2.2. The corresponding excitation cross section ratio measured by Geiger and Schröder (1969) is 2.7, by Chan *et al* (1993) is 2.6, by Zipf and McLaughlin (1978) is 2.9 and by Carter (1972) is 1.7. The last ratio was measured by high

resolution absorption spectroscopy and the set of former works were obtained by energy loss spectroscopy. The previously published cross section ratios from energy loss results must be viewed with caution, since the spectra did not resolve the structure from overlapping Rydberg and valence states.

ACKNOWLEDGMENTS

REFERENCES

Ajello J M, Ahmed S, Kanik I and Multari R 1995a, *Phys. Rev. Lett.* **75** 3261

Ajello J M, Ahmed S M and Liu X 1996a, *Phys. Rev. A* 53 2903.

Ajello J M, Kanik I, Ahmed S, Clarke J T 1995b, *J. Geophys. Res.* **100** 26,411.

Ajello J M, James G K, Franklin B O, and Shemansky D E 1989, *Phys. Rev. A,*
403524

Ajello J, Shemansky D, Kanik I, James, G, Liu, X Ahmed S and Ciocca M
1996b, *J. Elect. Spectrosc Rel. Phenom. 79 429*

Carter V 1972, *J. Chem. Phys. 56 4195*

Chan W F, Cooper G, Sodhi R and C. Brion 1993, *Chem. Phys.* **170** 81

Edwards S A, Tchang-Brillet W-UL, Roncin J-Y, Launay F and Rostas F 1995,
Planet. Space Sci. 43 67

Geiger J and Schröder B 1969, *J. Chem. Phys. 50 7*

Helm H, Hazell I and Bjerre N 1993, *Phys. Rev. A, 48 2762*

James G K, Ajello J M, Franklin B, and Shemansky D E 1990,}. *Phys. B. 23*
2055

Kam A W, Lawall J R, Lindsay M D, Pipkin F M, Short R C and Zhao, P
1989, *Phys. Rev. A, 40 1279*

Lefebvre-Brion H and Field R W, Perturbations in the Spectra of Diatomic
Molecules(Academic, Orlando, 1986) chap. 5, p. 244

Liu X, Ahmed S, Multari R, James G K and Ajello J M 1995, *Ap. J. Supp.*
101 *375.*

Roncin J-Y, Launay F, Subtil F and Yoshino K 1987a, *Planet. Space Sci.* **35** 1301.

Roncin J-Y, Launay F, Yoshino K 1987b, *Planet. Space Sci.* 35 267.

Shemansky D E, Kanik I and Ajello J M 1995, *Ap. J. 452 480*

Stahel D, Leoni "M and Dressier K 1983, *J. Chem. Phys. 79 2541*

Walter C W, Cosby P C and Helm H 1994, *Phys. Rev. A* **50 2930**

Yoshino K and Tanaka Y 1977, *J. Mol. Spectrosc.. 66 219*

Zipf E C and McLaughlin R W 1978, *Planet. Space Sci. 26 449.*

TABLE 2

ROTATIONAL LEVEL EIGENVECTOR COMPONENTS AND PREDISSOCIATION YIELDS FOR N_2 c' (v' =3 and 4)

J'	c'(v'=3) C_1^2 * b' % character	$\eta_P(J')$ predissoc. yield %	c'(v'=4) C_1^2 ** b' 70 character	$\eta_P(J')$ predissoc. yield %
0	0.267	31	0.25	10-20
1	0.268	31	0.25	10-20
2	0.270	35	0.26	10-20
3	0.274	36	0.27	10-20
4	0.278	24	0.29	10-20
5	0.284	30	0.31	23
6	0.292	45	0.34	19
7	0.302	46	0.37	44
8	0.315	34	0.40	52
9	0.330	51[+]	0.45	62+
10	0.348	51	0.50	87
11	0.371	59	0.46	78
12	0.399	49	0.62	93
13	0.431	63	0.68	87
14	0.470	39	0.75	93
15[^]	0.515	52	0.80	90
16[^]	0.566	52	0.84	90
17[^]	0.620	52	0.87	90
18[^]	0.676	52	0.90	90
19[^]	0.730	52	0.91	90
20"	0.780	52	0.92	90

* Edwards *et al* 1995.
** Helm *et al* 1993.

[+] Walter *et al* 1993.
[A] estimated, not observed.

TABLE 1
HIGH RESOLUTION STUDY OF c'(v'=3 and v'=4 PROGRESSIONS)

v"	$O_{v"}(1989)$ $(10^{-19}$ cm$^2)$	$O_{v"}(1996)$ $(10^{-19}$ cm$^2)$	$q_{v'=3,v"}(c\ ')$	$q_{v'=10,v"}(b\ ')$	ω_{exp}
o	0.40	0.35	2.5(-4)*	**3.5(-2)**	6.2(-2)
1	0.44	0.44	1.5(-2)	**6.8(-2)**	7.8(-2)
2	2.04	2.23	2.2(-1)	**4.2(-2)**	3.9(-1)
3	2.20	0.59	4.3(-1)	**2.1(-3)**	1.0(-1)
4	1.21	1.83	2.9(-1)	1.4(-2)	3.2(-1)
5	0.50	0.21	3.8(-2)	**3.5(-2)**	2.1(-2)
TOTALS	6.8	5.7			

v' = 4

v"	$Q_{v"}(1989)$ $(10^{-19}$ cm$^2)$	$Q_{v"}(1996)$ $(10^{-19}$ cm$^2)$	$q_{v'=4,v"}(c\ ')$	$q_{v'=13,v"}(b\ ')$	ω_{exp}
0	**2.50**	1.68	1.3(-5)	8.08(-2)	1.69(- 1)
1	**1.50**	0.82	1. 1(-3)	4.15(-2)	8.3(-2)
2	0.10	0.10	3.0(-2)	3.42(-4)	1 .0(-2)
3	**3.47**	3.28	2.6(-1)	3.1 (-2)	3.3(-1)
4	3.00	1.38	3.1(-1)	2.2(-2)	1.4(-1)
5	2.90	2.28	3.3(-1)	**2.2(-4)**	2.3(-1)
6	0.10	0.39	5.9(-2)	**2.2(-2)**	3.9(-2)
TOTALS	13.6	9.9			

* The number is paranthesis is the power of 10.

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TABLE OF FIGURES

FIGURE 1. High resolution laboratory spectrum of N_2 c' $^1\Sigma_u^+$ (4,3) and (3,2)) Rydberg bands in the EUV by electron impact excitation at 100 eV. The data are normalized to unity at the R-branch peak of the (4,3) band near 944.5 Å. The positions of the P-branch rotational lines are taken from Roncin and Launay (private communication, 1997).

FIGURE 2a. Composite spectrum of the two v" progressions for N_2 c' $^1\Sigma_u^+$ (v'=3 and v'=4)) Rydberg bands in the EUV by electron impact excitation at 100 eV from v" =0 and 1 for v'=3 and from v" =0 to 2 for v'=4. The intensities in Fig. 2a and Fig. 2b are normalized to 0.6 for the N_2 c' $^1\Sigma_u^+$ (4,3) band peak intensity.

FIGURE 2b. Composite spectrum of the two v" progressions for N_2 c' $^1\Sigma_u^+$ (v'=3 and v'=4)) Rydberg bands in the EUV by electron impact excitation at 100 eV from v" =2 to 4 for v'=3 and from v" =3 to 5 for v'=4. The intensities in Fig. 2a and Fig. 2b are normalized to 0.6 for the N_2 c' $^1\Sigma_u^+$ (4,3) band peak intensity.

FIGURE 3. Comparison of model and data from Fig. 1 for N_2 c' $^1\Sigma_u^+$ (4,3) and (3,2)) Rydberg bands at 100 eV. The predissociation yields for the model are normalized to the J' =9 value of Walter *et al* (1994) as shown in Table 2.

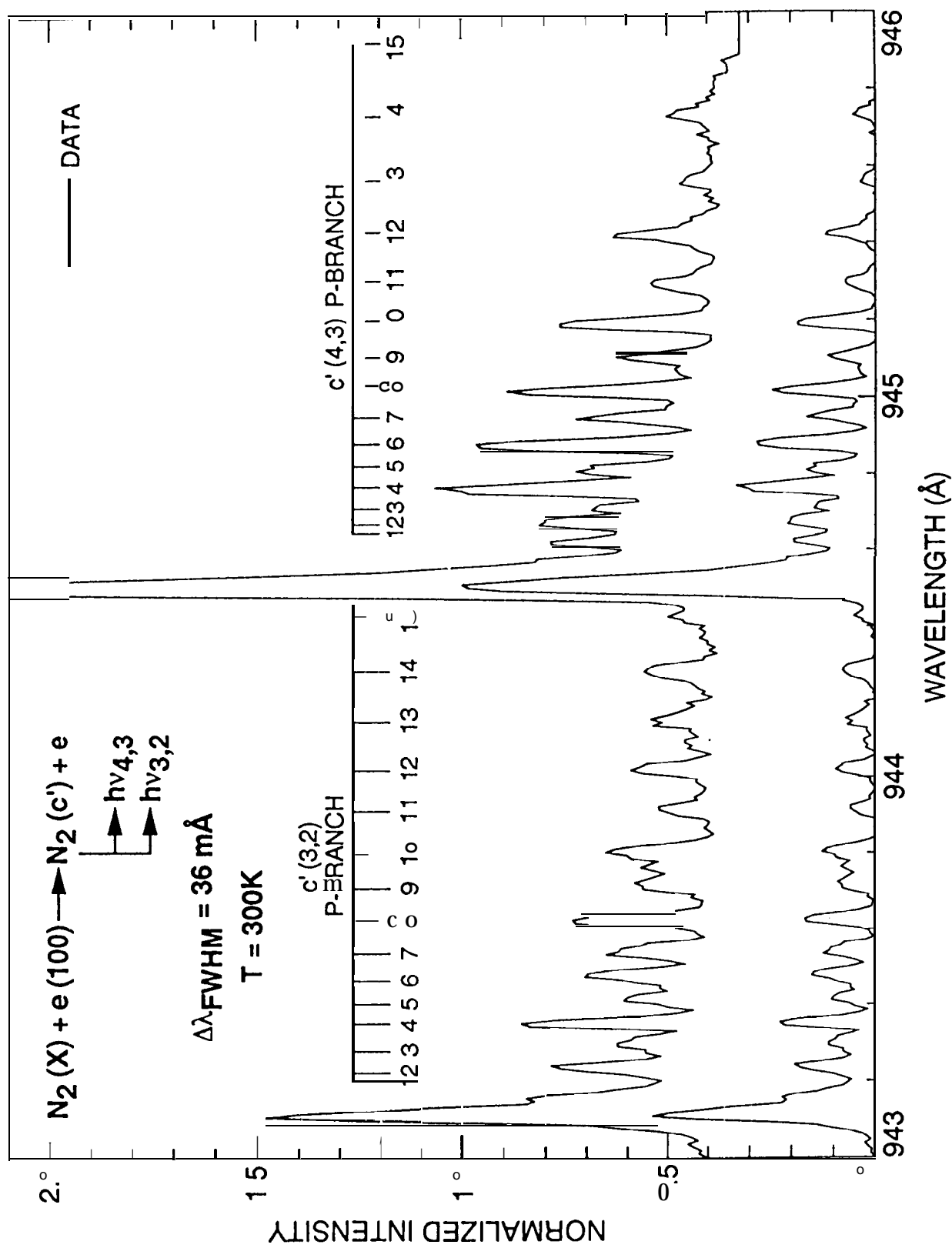FIGURE 4. Mean predissociation yield as a function of temperature for a Boltzmann distribution of ground state N_2 molecules.
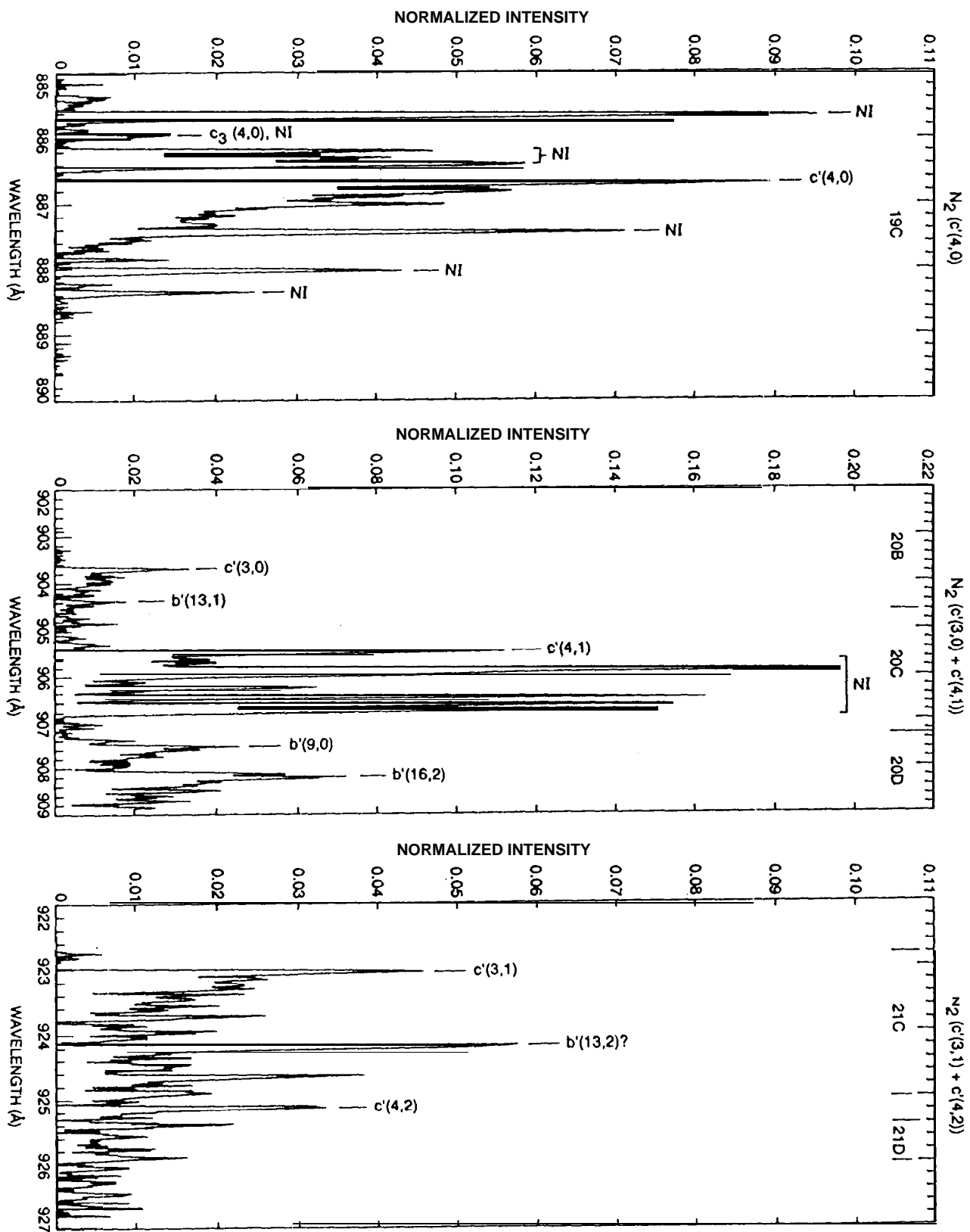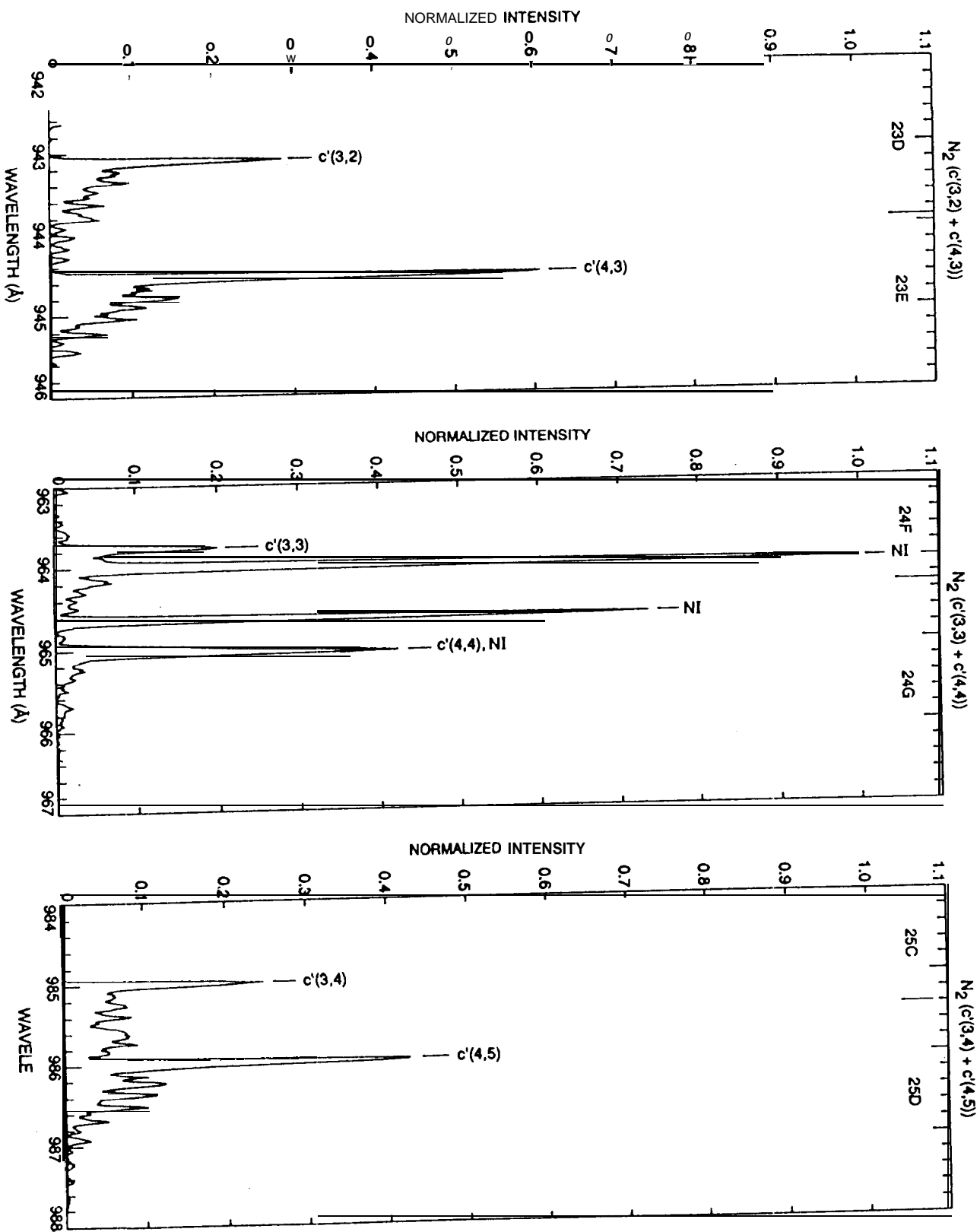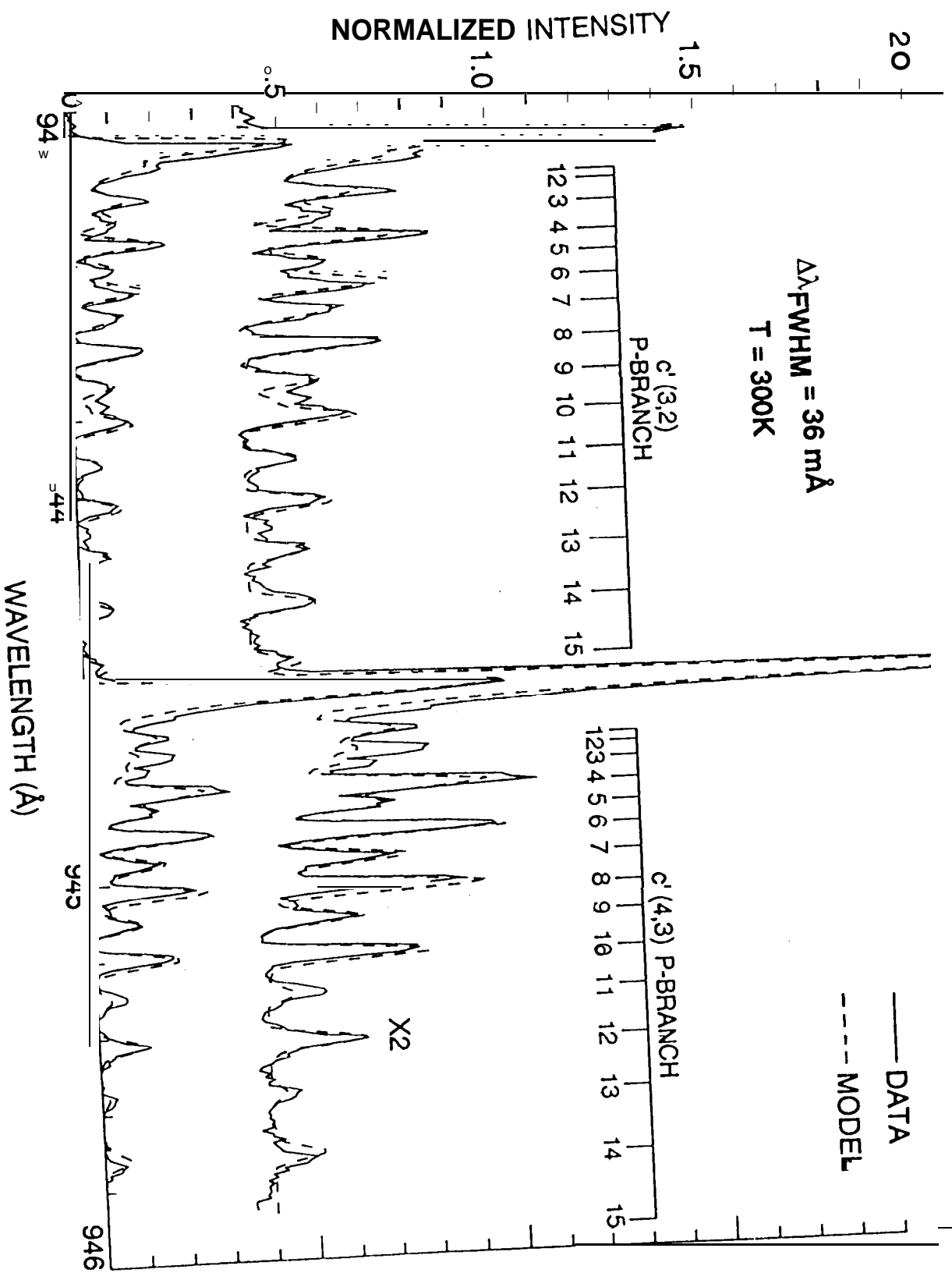
Fig. 1

Fig. 2a

Fig. 2b

Fig. 3

NORMALIZED INTENSITY

ΔλFWHM = 36 mÅ
T = 300K

c'(3,2)
P-BRANCH

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15

c'(4,3) P-BRANCH

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15

X2

WAVELENGTH (Å)

—— DATA
- - - - MODEL

Fig. 4